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**MICROBIOLOGICALLY INFLUENCED DEGRADATION OF CEMENT-SOLIDIFIED LOW-LEVEL RADIOACTIVE WASTE FORMS<sup>5</sup>**

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**ABSTRACT:** Because of its apparent structural integrity, cement has been widely used in the United States as a binder to solidify Class B and C low-level radioactive waste (LLW). However, the resulting cement preparations are susceptible to failure due to the actions of stress and environment. This paper contains information on three groups of microorganisms that are associated with the degradation of cement materials: sulfur-oxidizing bacteria (*Thiobacillus*), nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*), and heterotrophic bacteria, which produce organic acids. Preliminary work using laboratory- and vendor-manufactured, simulated waste forms exposed to thiobacilli has shown that microbiologically influenced degradation has the potential to severely compromise the structural integrity of ion-exchange resin and evaporator-bottoms waste that is solidified with cement. In addition, it was found that a significant percentage of calcium was leached from the treated waste forms. Also, the surface pH of the treated specimens was decreased to below 2. These conditions apparently contributed to the physical deterioration of simulated waste forms after 30 to 60 days of exposure.

**KEYWORDS:** cement, biocorrosion, thiobacilli, microbial degradation, low-level waste, solidification

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## INTRODUCTION

Evidence that microorganisms have been isolated in samples taken from LLW environments, combined with scientific data that demonstrate the existence of microorganisms under hostile conditions once thought to exclude them, have raised concerns that microbial activity at LLW disposal sites could affect the long-term stability of disposed waste. Because of apprehension over possible microbial effects on the waste and to ensure that LLW can be safely disposed for 300 to 500 years, the United States Nuclear Regulatory Commission (NRC) requires that microbial activity be tested to determine the stability of Class B and C wastes solidified in cement waste forms [10 CFR 61.56 (b)(1)]. To provide guidance to disposal vendors and nuclear station waste generators for implementing the stability requirements of 10 CFR Part 61, the NRC developed the Technical Position on Waste Form, Revision 1 (TPWFR1) [1]. This document details a specified set of required testing procedures and criteria, including several tests for determining the biodegradation properties of cement-solidified waste forms.

Concerns over the appropriateness of the TPWFR1 tests for microbial degradation of cement-solidified LLW were voiced [2]. It became apparent, during the deliberations, that improved tests would be required if meaningful information was to be obtained on microbial effects on cement-solidified wastes. A major difficulty identified was that the current testing procedures [1] did not adequately determine the bioeffects on cementitious materials. This was an obvious conclusion since the microorganisms used for the accelerated testing are not associated with cement degradation [3]. Further, it was pointed out that there are references in the literature that pinpoint microbial attack as one of the degradation processes that cement-solidified LLW is expected to encounter [4].

Because improved tests are needed, research is being conducted by the Idaho National Engineering Laboratory (INEL) for the NRC to provide data on the susceptibility of cement waste forms to microbiologically influenced degradation (MID), the rates at which degradation could occur, and the extent to which MID promotes leaching of radionuclides from the cement waste form. Data from this research will be used to develop standardized tests, which will replace those currently required by the TPWFR1 to assess the effects of microbial action on LLW forms.

The purpose of this paper is to provide information on MID of cementitious material and associated microorganisms, provide a description of a protocol for testing the MID susceptibility of cement-solidified LLW, and provide data from preliminary MID testing on both laboratory- and vendor-manufactured, simulated cement waste forms.

## DISCUSSION

Three groups of microorganisms contribute to the degradation of concrete integrity: sulfur-oxidizing bacteria, nitrifying bacteria, and some heterotrophic bacteria that produce organic acids. Species of each of these groups of organisms have been isolated from degraded concrete [5,6,7]. Biodegradation of concrete is thought to occur when ubiquitous environmental microorganisms produce mineral or organic acids that dissolve or disintegrate the cement matrix. The existence of these types of microorganisms at current and proposed LLW disposal sites is being investigated.

The particular mechanisms of biological acid attack are consistent with those that have been associated with chemical attack. Mineral acids such as sulfuric and nitric acids are extremely destructive and are known to destroy concrete at rates much faster than physical

weathering. Organic acids, both water-soluble, low-molecular-weight acids and insoluble, high-molecular-weight acids will also degrade concrete. Acetic, formic, and lactic acids have been shown to be very aggressive in attacking concrete [8]. It appears that two of the properties of concrete that determine its resistance to acid attack are the quality and amount of interstitial mortar (cement). Thus, cement content and waste loading would be expected to be variables in defining the degradation rate.

### Sulfur-Oxidizing Bacteria

Sulfur-oxidizing bacteria (genus Thiobacillus) are the microorganisms most often associated with the biological degradation of concrete structures. These organisms were found to be responsible for the catatrophic, biogenic sulfuric-acid attack of the Hamburg sewer system [9], and are now recognized as the causative factor in degradation of concrete sewer pipe [10,11]. Thiobacilli are chemoautotrophs that obtain energy by oxidizing reduced, inorganic sulfur sources such as elemental sulfur, thiosulfate, and polythionates, while assimilating carbon dioxide (CO<sub>2</sub>) as their only carbon source.

Ecologically, sulfur-oxidizing bacteria fill an important niche in the overall cycling of sulfur. In that cycle, there are several genera of bacteria that are capable of reducing oxidized forms of sulfur (organic sulfur compounds, inorganic sulfates) to sulfides and, under the proper conditions, to elemental sulfur. In turn, these reduced sulfur compounds then can readily become the substrate for the oxidizing bacteria that form sulfuric acid. It appears that regardless of the initial form of sulfur (reduced or oxidized), the natural sulfur cycle provides the potential for production of sulfuric acid. In general, it is assumed that sulfur oxidizers are ubiquitous in soil [12].

Thiobacilli are very versatile and can flourish under a range of environmental conditions. Islander [10] proposed that a natural succession of different species of thiobacilli are involved in the degradation of concrete in sewer systems and the production of acid mine drainage. The process appears to begin with the neutralization of calcium hydroxide, which is present in the concrete. When the concrete surface reaches a pH of near 9, Thiobacillus thioparus actively begins to oxidize available forms of reduced sulfur. Products from this process contribute to a continued decrease in surface pH. Soon, the species T. intermedius and T. novellus become active and the surface pH continues to decrease. As the pH falls to 6, T. neapolitanus is established. When the pH decreases to 3, T. thiooxidans becomes the dominate species, and the increasing acidity causes a drop of surface pH to near 1 or below. Finally dominating is a climax community consisting of T. thiooxidans and perhaps acidophilic heterotrophs capable of utilizing excreted organic waste. Because of the ability of T. thiooxidans to rapidly produce acid from available sources of sulfur, it has been suggested that its abundance is a better measure of degradation rate than the actual pH [13].

The above data suggest that, regardless of the initial populations of the various species of alkaline-tolerant, mesophilic, and acidophilic thiobacilli in an environment, once the process of sulfur oxidation begins, an extremely acidophilic species such as T. ferrooxidans or T. thiooxidans (requiring a pH of less than 3 for growth) will eventually become the dominant organism. The data indicate that regardless of the conditions that are simulated (in sewers or in soils from low-level radioactive disposal sites), T. thiooxidans and T. ferrooxidans appear to be the candidate organisms of choice for testing cementitious materials.

### Nitrifying Bacteria

The second group of microorganisms known to promote concrete degradation are the nitrifying bacteria. These bacteria (Nitrosomonas and Nitrobacter), like the sulfur oxidizers, are chemoautotrophs. They obtain energy through the oxidation of inorganic nitrogen compounds. These organisms have been isolated from a variety of soils, and many species of the ammonium oxidizers appear to be ubiquitous, becoming active under suitable conditions [14]. They are an important part of the biological cycling of nitrogen within the ecosystem. Neutral-to-alkaline soils have the largest populations of nitrifying bacteria; however, optimum pH for individual isolates varies from 6.6 to 8.0 or higher.

Both the ammonium oxidizer Nitrosomonas and the nitrite oxidizer Nitrobacter have been isolated from degraded concrete. They have been demonstrated to be active in biological, nitric-acid degradation of concrete during controlled experiments [15,16]. Bock et al. [6] found that nitrifiers were the most abundant organisms deteriorating building stone. The outermost layers to a depth of 5 mm were heavily contaminated with these bacteria. The stone surface had a pH of 5, which was attributable to the presence of nitric acid.

Evidence for sequential growth of these organisms on concrete is not as well documented as it is for the sulfur-oxidizing bacteria. However, in controlled experiments (using a simulation chamber), it was found that pure cultures of both Nitrosomonas and Nitrobacter that were inoculated on concrete blocks produced about 14 mL of 65% nitric acid per block per year [5]. This was sufficient acid to dissolve the concrete and produce the breakdown product calcium nitrate.

### Heterotrophic Bacteria

The third group of microorganisms that degrade concrete are heterotrophic bacteria, which can be found everywhere and can produce organic acids through the assimilation of organic carbon compounds. Organic acids such as lactic, citric, gluconic, malic, and many others are byproducts of the metabolism of these microbes. A variety of organic acids are produced on an industrial scale through the metabolic activity of these microbes. Several types of these organisms, collected from a wide range of environments, are known to use an organic acid mechanism for the active extraction of phosphate from phosphate ores [17]. They are known to promote acid conditions to less than pH 3.

Because of their diversity, heterotrophs can exist under a much wider range of environmental conditions than either the sulfur oxidizers or nitrifying bacteria. While their abundance increases with the quantity of organic matter, they can be expected in almost any environment where even a minute carbon source exists. The amount of acid that they are capable of producing depends on the organisms responsible and the environment in which they are growing. The phenomenon of heterotrophic biodegradation of concrete has not been well studied. Karavaiko [7] examined heterotrophs in relation to affects on concrete and suggested that a community of organisms, not an individual representative, is responsible for the process. It has been reported that at least 42 microbiological species have been identified in the various environments where concrete degradation has occurred [18].

In work conducted to determine the microbiology associated with the English nuclear waste disposal effort [19], it was discovered that a wide diversity of heterotrophic microorganisms could be isolated from simulated, cement-solidified, plutonium-contaminated materials. Under culturing conditions, it was determined that many of these microbes were capable of growing in the alkaline conditions (pH 11) common on the

surface of concrete. Unfortunately, the studies were not carried out over a sufficient period of time to determine if growth of the organisms affected the integrity of the concrete.

Studies on the effects of heterotrophic degradation of cement-solidified LLW have been conducted by the French (personal communication with N. Langomazino, 1990). Microorganisms used in those studies were isolated in a microbial growth media containing concrete powder and common soil (the initial source of microbes). Several species of microbes were isolated by this method. They all had in common the ability to maintain good growth in an alkaline media (pH 9), were able to grow and multiply in the presence of cement, and apparently produced organic acids. A fungus and the bacterium Pseudomonas cepacia were selected for the concrete degradation studies. The degradation studies were conducted by exposing samples of concrete to a continuous source of pregrown microbes for periods of up to 1 year. Samples of concrete were retrieved for evaluation at 1-month intervals. These samples were evaluated for strength, weight loss, loss of structural material (calcium and aluminum) and porosity, and for changes in the structural matrix (x-ray diffraction). After 5 months, it was determined that those samples exposed to the bacteria had lost 12% of their weight (on a dry weight basis) while those exposed to the fungus had a weight loss of 10%. In addition, the samples had a 5% decrease in calcium. The loss of calcium was not correlated with the amount of available organic acid, which indicates that organic chelation of calcium was not the only mechanism responsible for the process of calcium depletion. At the end of 7 months, there had been an 11% increase in porosity in the samples. It was speculated that the increased porosity was directly related to the loss of calcium hydroxide [Ca(OH)<sub>2</sub>] crystals. By the end of 11 months, there had been a 50 to 85% loss of Ca(OH)<sub>2</sub> in the treated concrete samples, as compared to control samples not exposed to the microbes, with a resulting 80% loss of compressive strength in the treated samples.

The French work was continued with studies involving the exposure of concrete samples to organic-acid-producing fungi under conditions that encouraged fungal growth on the specimens [20]. Results from a 2-year period of time demonstrated that the organic-acid-producing fungi were responsible for a significant loss of calcium from a defined leach layer of 0.2 cm. The associated pH of the solution surrounding the test specimens was in the mid 4's.

#### TEST METHODOLOGY

It has been determined that standardized biodegradation tests such as the ASTM Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi (G21-70) and ASTM Standard Practice for Determining Resistance of Plastic to Bacteria (G22-76) are not applicable for use in determining the effect of MID on cement-solidified LLW. Therefore, it has been necessary to begin devising and evaluating procedures that provide candidate bacteria from the three different genera, according to the following criteria: These bacteria must be known to degrade concrete, have optimum conditions of growth, exposure to a test specimen, and sufficient reaction time to promote degradation. The test method that has been developed provides a candidate bacteria with optimum growth conditions and exposure to the cement test specimen. This has been accomplished through the use of a microbial propagation system (continuous flow bioreactor) coupled with a specimen exposure chamber (Fig. 1). With this system, the bacteria can be grown under optimum conditions of nutrients and temperature. The microbes can then be introduced to the test specimens by several methods including continual perfusion. Using this method, the specimen is completely immersed in a continual flow of microbially produced biomass and exudates collectively known as lixiviant.

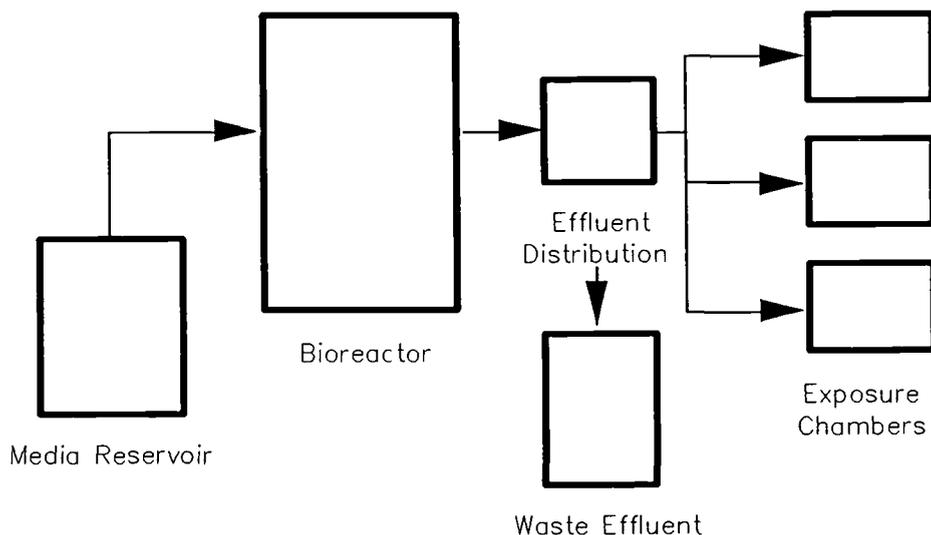


FIG. 1--Schematic of test apparatus with a continuous flow bioreactor for microbial propagation coupled with a specimen exposure chamber.

The only tests reported in this paper were conducted with the continual perfusion method using lixiviant produced by the candidate microbes *T. thiooxidans* and *T. ferrooxidans*. Other studies using different exposure methods and nitrifying and heterotrophic bacteria will be reported in the future. In the continual perfusion method, each of the bacteria were grown under continuous conditions in separate bioreactors. Test specimens used in the studies were simulated cement waste forms with materials similar to those found in actual cement waste forms from commercial power reactors. Two sets of simulated waste forms were evaluated. They included those fabricated at our laboratory (INEL) and others provided by a vendor. The INEL waste forms were fabricated with Portland Type II cement and contained either the equivalent salts contained in some evaporator bottoms or ion-exchange resins but no radioactivity (Fig. 2). In addition, the ASTM Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (C109-90) was used to formulate control cement specimens. All of these specimens were molded as 1.8 x 2.2 cm cylinders. The vendor's process and formulations for waste form production are proprietary. The vendor used its methods to produce simulated waste forms from both ion-exchange resin and evaporator bottoms (salts). Before use, these waste forms were cut into pie-shaped specimens 3 cm wide, 2.5 cm long, and 1 cm thick.

A test system was devised in which the simulated waste form specimens of evaporator bottoms and ion-exchange resin, along with the ASTM control, could be exposed to lixiviant produced by *T. thiooxidans* and *T. ferrooxidans* as well as the bacteria-free (sterile) medium used to support microbial growth. The intended duration of this continuous exposure test was 60 days. However, the vendor's waste forms were exposed for only 30 days. During the test, samples of the liquid that had come in contact with the INEL cement specimens (effluent) were collected and analyzed for calcium content and pH. In the case of the vendor's specimens, the effluent was analyzed for calcium, iron, aluminum, magnesium, and silica. At the conclusion of the test, the specimens were collected for physical examination to determine the extent of MID.

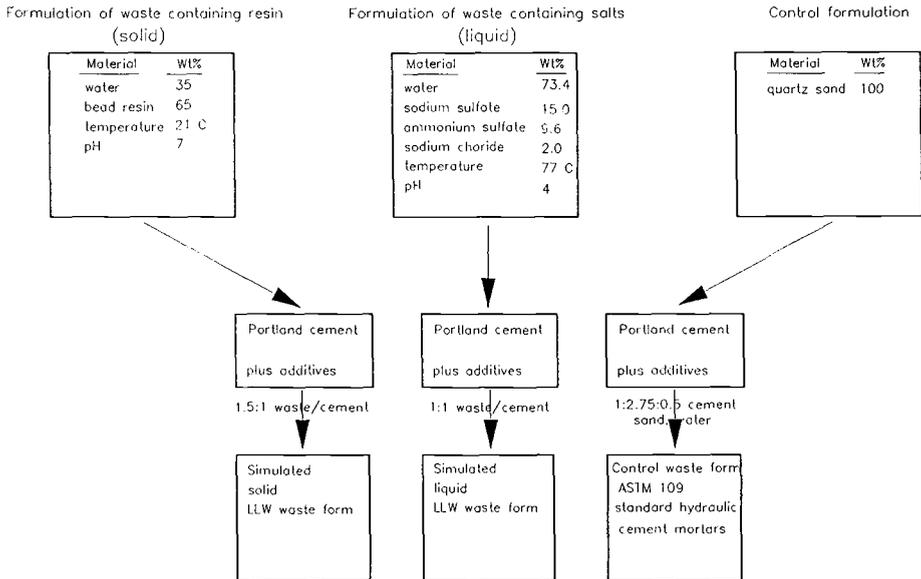


FIG. 2--Test specimen formulations.

## RESULTS

The extent of MID affecting the ASTM control cement specimens after 60 days of exposure to thiobacilli lixiviant can be seen in Fig. 3. This figure shows the ASTM control immersed for 60 days in the sterile medium (Fig. 3a), the ASTM control with *T. ferrooxidans* lixiviant (Fig. 3b), and the ASTM control with *T. thiooxidans* lixiviant (Fig. 3c). The same sequence is shown in Figs. 4 and 5 for the INEL-simulated cement-loaded evaporator bottoms (salts) and ion-exchange resin, respectively. Notice that there is little or no apparent physical damage to the ASTM control and evaporator-bottoms waste form exposed to the sterile medium (Figs. 3a and 4a), while there is extensive damage in the form of spalling, material loss, and lighting of color to those specimens that were in contact with the thiobacilli lixiviants (Figs. 3b, 3c, 4b, and 4c). In the case of the ion-exchange-loaded waste forms (Fig. 5), physical damage is seen with all the specimens. It is not uncommon for these types of specimens to disintegrate, in even distilled water, due to swelling of the resin beads. However, what should be noted from Fig. 5 is that the waste form exposed to the sterile medium (Fig. 5a) still retains a cement matrix in which resin beads are firmly imbedded. The other two waste forms exposed to thiobacilli lixiviants, however, have lost their cement matrix as noted by the appearance of loose resin beads (Figs. 5b and 5c).

Chemical evidence of the effect of MID is exhibited by the extensive loss of calcium from the INEL-simulated waste forms exposed to thiobacilli lixiviant. The quantities of calcium removed during exposure to the two lixiviants and the sterile medium can be seen in Fig. 6. The calcium lost from the specimens that were exposed to the *T. ferrooxidans* lixiviant ranged from 30% for the ASTM control to 89% for the ion-exchange load waste form. For the *T. thiooxidans* lixiviant and sterile medium, the corresponding values were 20 to 59% and 20 to 12%, respectively. These data support the assumption that loss of the

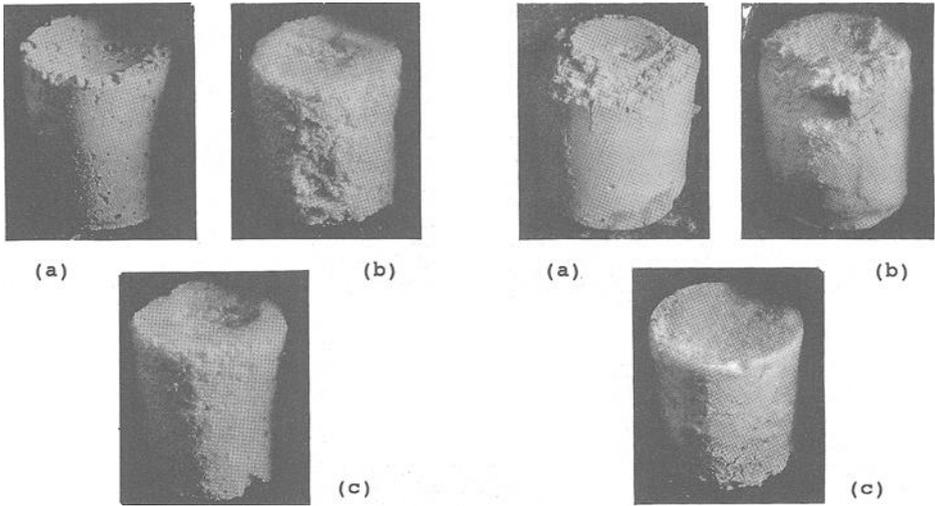


FIG. 3--ASTM control cement waste form after being immersed 60 days in (a) sterile media, (b) T. ferrooxidans lixiviant, and (c) T. thiooxidans lixiviant.

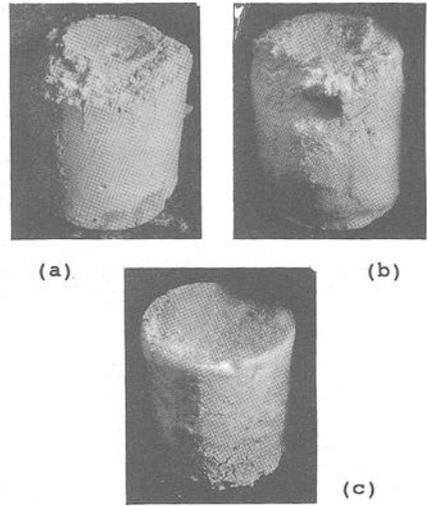


FIG. 4--INEL-simulated cement waste forms loaded with evaporator bottoms after being immersed for 60 days in (a) sterile media, (b) T. ferrooxidans lixiviant, and (c) T. thiooxidans lixiviant.

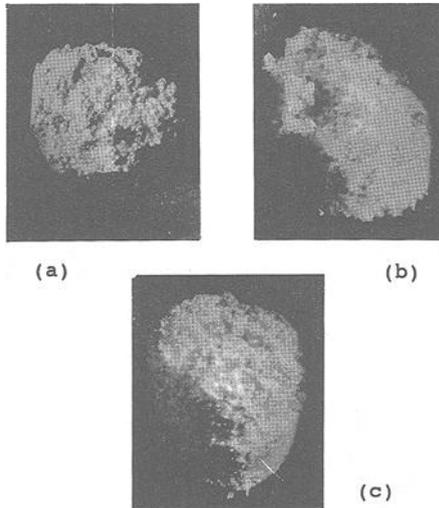


FIG. 5--INEL-simulated cement waste forms loaded with ion-exchange resin after being immersed for 60 days in (a) sterile media, (b) T. ferrooxidans lixiviant, and (c) T. thiooxidans lixiviant.

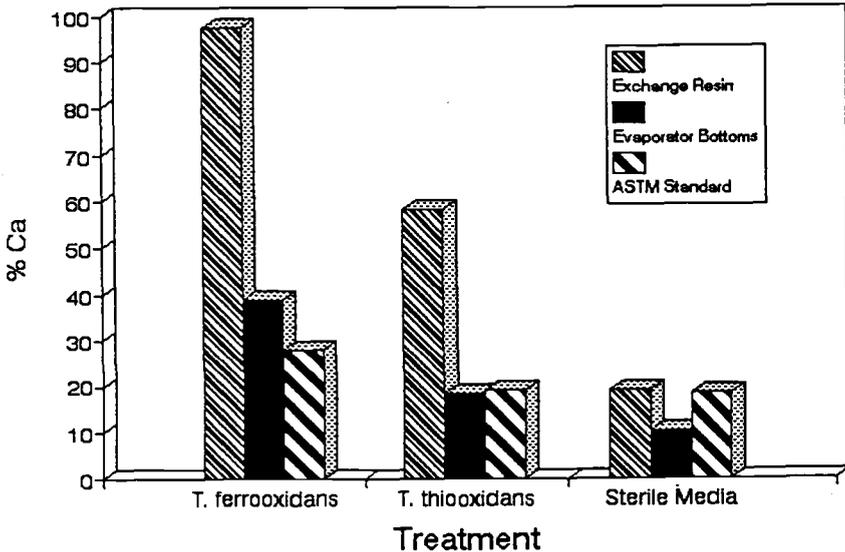


FIG. 6--Percent calcium leached from INEL-simulated waste forms loaded with evaporator bottoms and ion-exchange resin and ASTM control cement waste forms after being immersed 60 days in sterile media or microbially produced lixiviant.

cement matrix contributed to the deterioration of the simulated waste forms. The pH of the INEL waste form effluent was determined. These data show that the waste forms had little effect on moderating the acid environment supplied by the two lixiviants (Fig. 7). The pHs of these effluents were consistently 2 or lower during the course of the test. On the other hand, considerable buffering was noted for the sterile-medium effluent. The initial effluent pH was as high as 9 and then decreased over time to about 3.2, which was the pH of the fresh, sterile medium. The effect of a continual supply of low-pH lixiviants that are biologically produced can be seen in the resulting surface pH of the test specimens (as determined by pH-sensitive paper strips) (Table 1). Note that those specimens in contact with a lixiviant had very low surface pHs as compared to the sterile medium treated or untreated specimens. Low pHs in these ranges are known to cause damage to cement materials.

As was mentioned earlier, the duration of the second study using the vendor-supplied, simulated cement waste forms was limited to 30 days. It was found that neither of the specimens exposed to sterile media appeared to have any damage (Figs. 8a and 9a). However, the simulated evaporator-bottoms waste form immersed in *T. ferrooxidans* lixiviant appeared to have swelled and was extensively damaged (Figure 8b). Also, exposure of the same type of waste form to the *T. thiooxidans* lixiviant caused similar swelling, with most of the physical damage appearing on the specimen's edges (Fig. 8c). Both of the vendor-supplied, simulated ion-exchange resin waste forms were extensively damaged by the bacteria lixiviants (Figs. 9b and 9c). In comparison, these results were similar to those obtained from the evaluation of the INEL-simulated waste forms. That is, the specimens appeared to have lost much of their cement matrix, which resulted in the resin beads being loosely attached to the eroded surface.

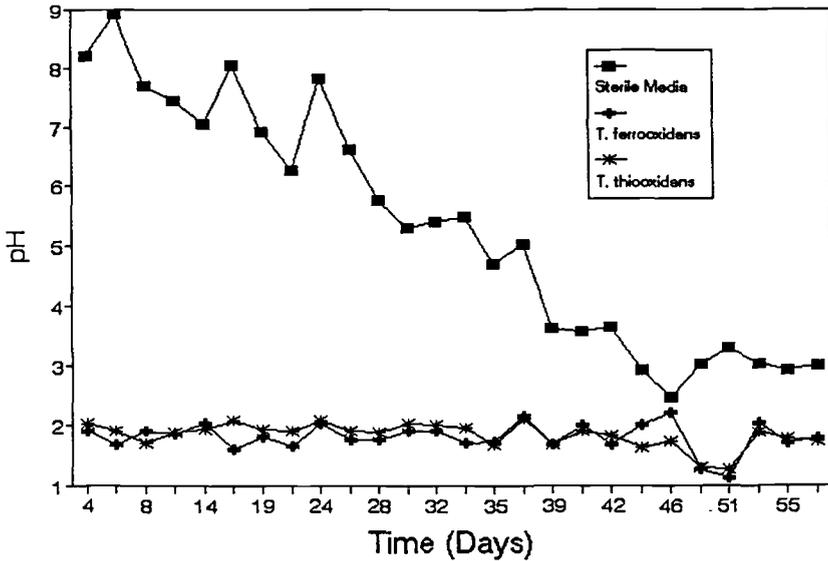


FIG. 7--pH of exposure chamber effluent (produced from lixiviant in contact with INEL-simulated cement waste forms) averaged across waste form type.

TABLE 1--Surface pH of INEL-simulated cement waste forms before and after immersion for 60 days in sterile media or microbially produced lixiviant.

Treatment	Simulated cement waste forms		
	Exchange resin, pH	Evaporator bottoms, pH	ASTM standard, pH
Untreated	9	13	11.5
Sterile media	10	10	7
T. ferrooxidans	0.5	4.5	3.0
T. thiooxidans	1.0	1.5	3.0

As was previously mentioned, effluent from this study were analyzed for the presence of calcium, aluminum, silica, iron, and magnesium. As with the INEL-fabricated waste forms, it was found that calcium was leached from the vendor-supplied waste forms as a result of exposure to the various liquids (Fig. 10). The amount leached from the exchange resin waste forms ranged from 17 to 46%, with a 7 to 29% loss from the evaporator-bottoms specimens. Once again, those waste forms exposed to the bacterial lixiviants lost substantially more calcium than those treated with only the sterile media. Calcium loss from the waste forms was practically doubled by the presence of the *T. ferrooxidans* lixiviant and was more than tripled by the *T. thiooxidans* treatment.

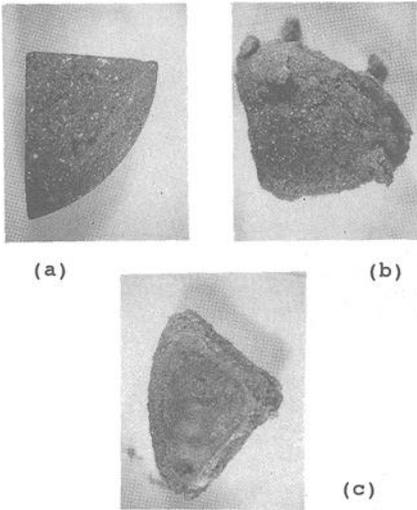


FIG. 8--Vendor-supplied simulated cement waste forms loaded with evaporator bottoms after being immersed 30 days in (a) sterile media, (b) T. ferrooxidans lixiviant, and (c) T. thiooxidans lixiviant.

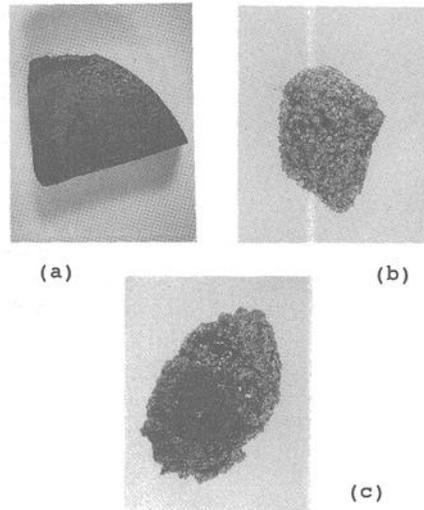


FIG. 9--Vendor-supplied simulated cement waste forms loaded with ion-exchange resin after being immersed 30 days in (a) sterile media, (b) T. ferrooxidans lixiviant, and (c) T. thiooxidans lixiviant.

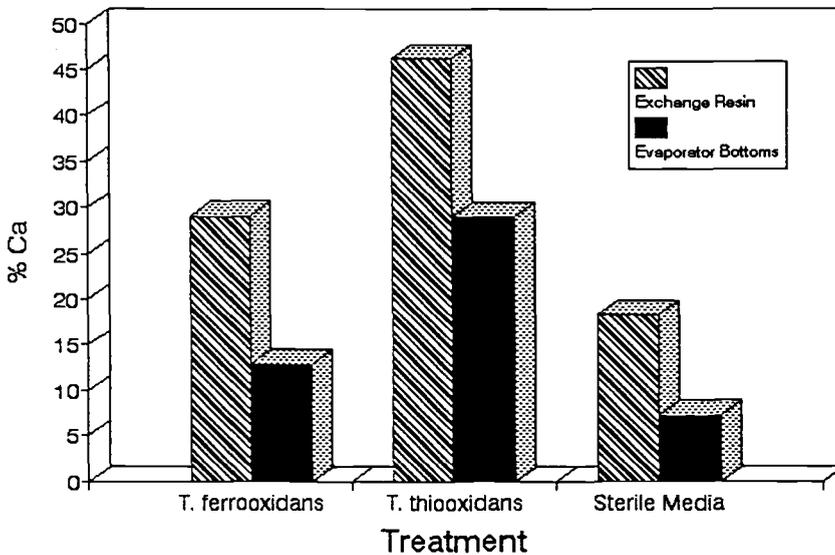


FIG. 10--Percent calcium leached from the vendor-supplied simulated waste forms loaded with evaporator bottoms and ion-exchange resin after being immersed 30 days in sterile media or microbially produced lixiviant.

Loss of aluminum occurred only from those specimens exposed to the thiobacilli lixiviant (Fig. 11). Amounts leached from the two types of simulated waste forms were similar within each treatment and ranged from 9 to 14% for the *T. ferrooxidans* treatment and from 19 to 21% for specimens exposed to the *T. thiooxidans* lixiviant. Only a minimal amount of silica (less than 0.2%) was removed from specimens regardless of the treatment (Fig. 12). While the initial, total quantities of iron and magnesium were not determined for the vendor-supplied, simulated waste forms, these elements were shown to be leached from the specimens (Figs. 13 and 14). More iron was leached from those specimens exposed to the bacterial lixiviant than from the sterile media. Simulated waste forms containing exchange resin had a larger quantity of iron removed than did those waste forms that contained evaporator-bottoms material. Also, leaching was more apparent with the *T. thiooxidans* lixiviant. The magnesium data (Fig. 14) were surprising since it was shown that more of the element, regardless of waste form type, was in the sterile media effluent than in the bacterial lixiviants. This was a curious finding for which no explanation was apparent.

As in the case of the INEL-simulated waste forms, data on effluent pH showed that the specimens had little effect on moderating the acid environment imposed by the thiobacilli lixiviants. Over the course of the study, the average pH of the two lixiviants remained near 2 (Fig. 15). The pH of the sterile media exposed to the vendor waste forms showed that during the first 7 days, the pH remained at the ambient level of near 3. After this time, the pH began to increase to 6 and 7. These data are significantly different than those of the INEL material (Fig. 7). It appears that the vendor waste forms contributed little to the initial buffering of the sterile media. Why buffering of the sterile media occurred later in the study was not ascertained.

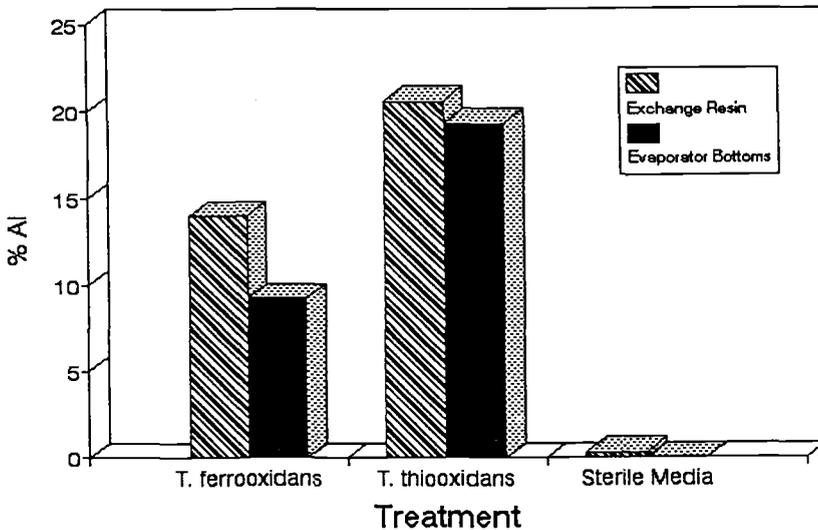


FIG. 11--Percent aluminum leached from the vendor-supplied simulated waste forms loaded with evaporator bottoms and ion-exchange resin after being immersed 30 days in sterile media or microbially produced lixiviant.

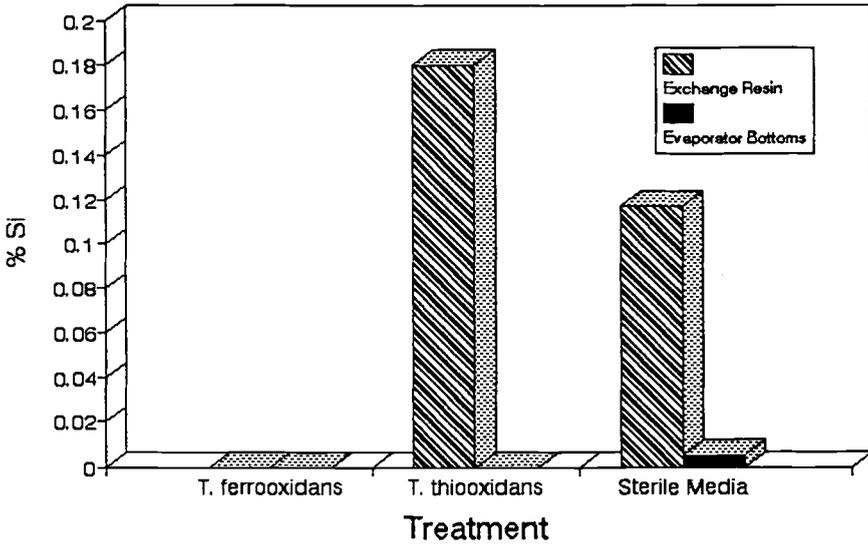


FIG. 12--Percent silica leached from the vendor-supplied simulated waste forms loaded with evaporator bottoms and ion-exchange resin after being immersed 30 days in sterile media or microbially produced lixiviant.

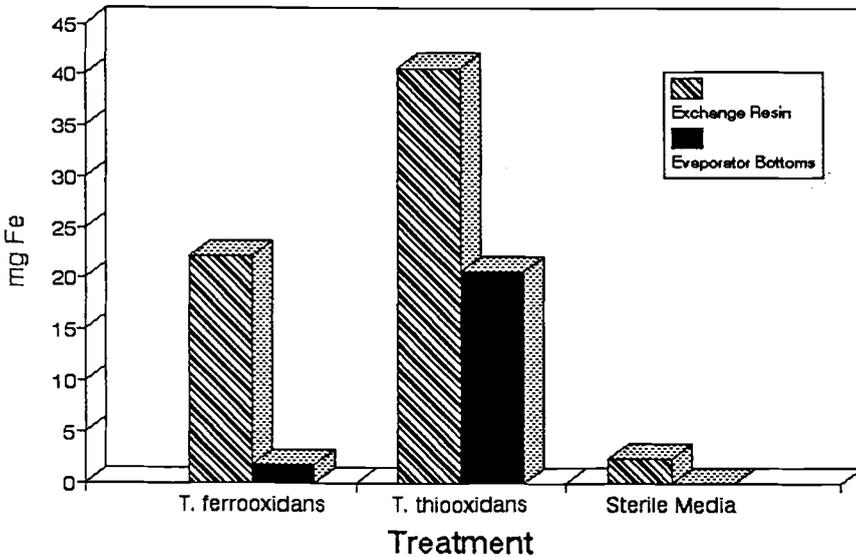


FIG. 13--Quantities of iron leached from the vendor-supplied simulated waste forms loaded with evaporator bottoms and ion-exchange resin after being immersed 30 days in sterile media or microbially produced lixiviant.

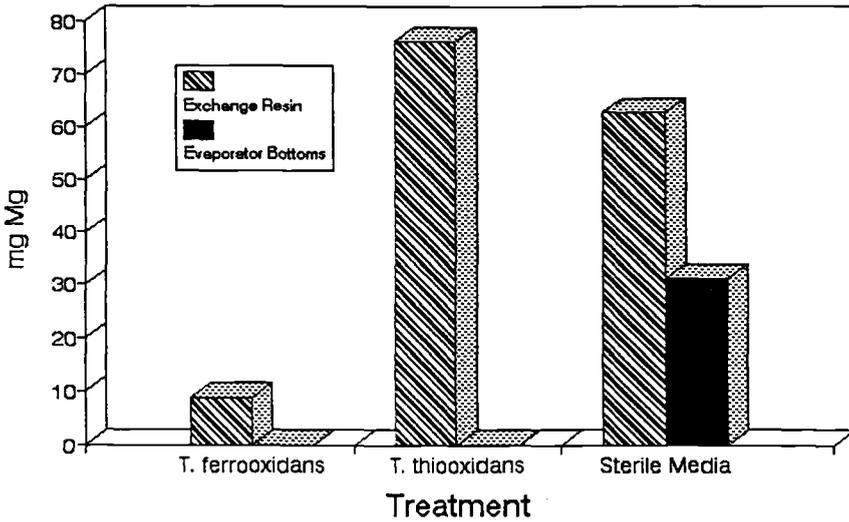


FIG. 14--Quantities of magnesium leached from the vendor-supplied simulated waste forms loaded with evaporator bottoms and ion-exchange resin after being immersed 30 days in sterile media or microbially produced lixiviant.

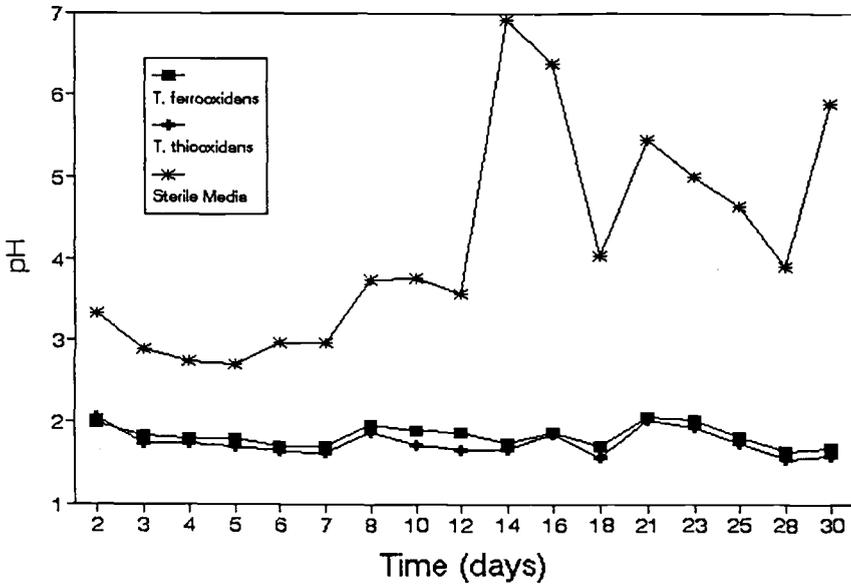


FIG. 15--pH of exposure chamber effluent (produced from lixiviant in contact with vendor supplied simulated waste forms) averaged across waste form type.

The continued exposure of waste forms to the thiobacilli lixiviants had a marked influence on their final surface pHs. Table 2 shows that the normal surface pH of the untreated specimens was decreased from alkalinity (pHs of 9 and 13) to extreme acidity (pHs of 1 to 3). While the sterile media had some effect, the surface pHs remained alkaline. These results are similar to those obtained from the INEL materials.

TABLE 2--Surface pH of vendor-supplied, simulated cement waste forms, before and after immersion for 30 days in sterile media or microbially produced lixiviant.

Treatment	Exchange resin, pH	Evaporator bottoms, pH
Untreated	9	13
Sterile media	9.5	8.5
T. ferrooxidans	1.0	3.0
T. thiooxidans	3.0	3.0

## CONCLUSIONS

Data from the work presented in this paper show that LLW solidified with cement is susceptible to MID. In this study, the cementitious materials were substantially damaged by the aggressive action of thiobacilli lixiviants. The physical damage to INEL- and vendor-prepared simulated waste forms (both those containing exchange resin or evaporator bottoms) demonstrates that the stability of cement-solidified waste forms could be compromised by microbial action. From this work, it appears that growth substrates naturally present in the disposal environment or provided by the contents of the waste form, such as sulfur or reduced sulfur compounds, could promote the degradation of waste forms.

A possible mode of attack appears to be through a process that lowers the surface pH of the cementitious material. While this is occurring, calcium is removed from the material. Since binding strength of the cement primarily relies on calcium content, the loss of calcium results in a decrease of waste form integrity. The data indicate that the severity of the attack could be moderated by formulation. That is, test specimens containing less simulated waste would be more resistant to degradation than specimens with higher waste loadings. There are not enough data yet to make comparisons between the formulations that were used to manufacture the waste forms.

Future work includes the development of additional methods for exposing simulated cement waste forms to not only the sulfur-oxidizing bacteria but also to nitrifying and heterotrophic bacteria. Exposure methods will include intermittent immersion and exposure to lixiviant mist. Eventually, actual cement-solidified waste forms will be tested for durability and radionuclide leaching.

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